Porosity Development in Activated Carbon from Palm Kernel and Coconut Shell by Chemical Activation Method

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Abstract

Several series of activated carbons have been prepared by chemical activation with phosphoric acid from palm kernel and coconut shells to study the effect of preparation variables such as precursor, precursor size, pretreatment, impregnation condition and ratio and finally the carbonization temperature on specific surface area and pore distribution of the resulting active carbon. Both precursors showed similar N_2 adsorption isotherms, an upward deviation at high relative pressure, revealing the presence of mesorpores when carbonized at 500^0 C with H_3PO_4. The bigger hysteresis loop indicates higher mesoporosity in coconut shell derived carbon whereas palm kernel shell derived carbon showed a higher macroporosity nature.

Prolong sinking of the precursor in H_3PO_4 impregnation solution followed by carbonization at moderate temperature (450-500^0 C) produces carbon of high surface area with a higher macroporosity. The lowering of precursor size favors micropore development and semi-drying of the impregnation chemical prior to carbonization diminishes the macroporosity to a great extent. Thus an appropriate choice of preparation variables enables us to produce high surface area of micro and mesoporous activated carbon.

Keywords: Activated carbon, chemical activation, phosphoric acid, palm kernel, coconut shell.

Introduction

Almost any carbonaceous material can be converted into activated carbon[1] whether it is occurring naturally such as coal and lignocellulosic materials or prepared synthetically such as organic polymers. One must tailor the activated carbon with high micro, mesopore volume and large specific surface area for application in specific use. The development of pores and their distribution mainly depends upon the precursor type and the process of preparation. The resources of raw materials used for producing activated carbons are limited; the attempts to find new raw materials for this purpose are of great interest.

The beneficial use of agricultural wastes in activated carbon industries would be the best economy favored and environmental friendly solution to their great disposal problem. Huge amounts of palm kernel and coconut shells are produced as agricultural wastes in Malaysia. The utilization of these shells as carbon precursor is very promising. The object of this study is to focus the effect of preparation variables on specific surface area and pore distributions for producing micro and mesoporous carbon with highly developed surface area from local raw materials such as palm kernel and coconut shells using H_3PO_4 as activating agent. Chemical activation with H_3PO_4 is chosen for: ease of carbonization, lower temperature, one step process which can be performed even in a muffle furnace[2]; eliminating N_2 supply by a natural draft induced air inside furnace; maximizing adsorptive capacity and bulk density and achieving high product yield.

Material and Methods

Preparation of raw material: Palm kernel and coconut shells (P and C) were collected from local palm oil processing factory and market places respectively and then washed with tap water to remove dirt followed by drying in the sunlight. The dried palm kernel and coconut shells were crushed and sieved to two selected particle sizes, ranging 1.18- 2.36 and 0.60-1.18 mm. Finally, crushed particles were washed with acids as called pretreatment. Pretreatment (SW or PW) was conducted by soaking the raw materials in either of 30% H_2SO_4 or 30% H_3PO_4 solution in a bucket for a period of 24 hours and then by washing with distilled water to free acid and by subsequent drying to eliminate moisture.

Preparation of activated carbon: Prior to carbonization, the prepared raw materials whether pretreated (PSW/ CSW/ PPW/ CPW) or un-pretreated (CR) were impregnated with varying conditions and amounts of H_3PO_4 solution (PSW-P/CSW-P/CPW-P/CR-P etc). Carbonizations were carried out in a porcelain casserole, placed in a muffle furnace at different temperatures, 400, 450, 500 and 700^0 C, with a constant, one hour, hold time. After carbonization, products (PSW-P-500 etc.) were thoroughly washed with distilled water to about neutrality and then dried in an oven overnight at 110^0 C.

Characterization of Prepared Carbon

Determination of textural characteristic: The porous structure of prepared carbons was analyzed by N_2 adsorption-desorption at 77K with an accelerated surface area and porosimeter, ASAP 2010 Micromeritics. The Brunauer, Emmett and Teller (BET) equation and t-plot method were used to calculate surface area and microporosity. The single point total pore volume was measured from the amount of nitrogen adsorbed at the

relative pressure of 0.99. The mesopore volume is calculated from cumulative pore volume within the range of pore diameter 2 – 50 nm using BJH adsorption pore distribution. Then, macropore volume = Single point total pore volume – (micropore + mesopore) volume and pore distribution (%) = (specific pore volume / total pore volume) × 100.

Surface Morphology Characterization: Scanning Electron Microscopy (SEM) was used.

Results and Discussion

Evaluation of N_2 Adsorption and Porosity

Effect of precursor type: Effect of precursor type was studied from palm kernel and coconut shells derived carbons PSW-P-500 and CSW-P-500. They showed similar adsorption isotherms, type I with an upward deviation at high relative pressure, revealing the presence of mesopores. The broader knee and bigger hysteresis of coconut shell carbon result from the co-existence of micro- and mesopores in larger amounts than that of palm kernel shell derived carbon. As the BET surface area and total pore volume of both carbons are nearly same (ca. 1050 m^2/g and 0.6 cm^3/g respectively), the formation of macropores in PSW-P-500 is to be larger. The calculated macropore distributions in palm and coconut shell derived carbons are 47 and 20% respectively.

When viewed through Scanning Electron Microscope (SEM), highly cracked surfaces were observed in the palm kernel shell carbon. The development of macropores seems to be inevitable in preparing activated carbon from palm kernel shell as Daud et al[3] observed a rapid development of macropore volume with increasing burn-off which reaches to the maximum at a burn-off of about 30-50%. Besides, it is also observed from this experiment that palm shells are more vulnerable than that of coconut.

Effect of pretreatment: "The acid-treatment enhances processes which prevent the evolution of large quantities of volatile substances in the carbonization process, as a result of which active carbon granules of high mechanical strength are obtained" [4]. As palm kernel and coconut shells contain highly volatile matter (68.8 and 72.8 wt. % respectively), pretreatment plays an important role in governing the mechanical strength, yield and pore development of resulting carbon. The highest macroporosity (54%) is observed in a carbon CR-P-500, that was prepared from un-pretreated coconut shell precursor. The yield is achieved a little lower (37%) because of higher evolution of volatile matter.

Thus it is observed that skip of an acid-pretreatment step makes the material weak in mechanical strength and thus highly vulnerable. The very poor micropore distribution (7%) in CR-P-500 might be resulted from filling out the pores by disorganized carbon or from collapsing the walls of micropores. Pretreatments of raw coconut shell with H_2SO_4 and H_3PO_4 were carried out to study the effect of particular acid on pore development in resulting carbons, CSW-P-500 and CPW-P-500 respectively. The highest BET surface area (1491 m^2/g) was obtained in carbon prepared from H_3PO_4 pretreated precursor although it has a little high macroporosity (31%). Pretreatment with H_3PO_4 restricts the process of volatile evolution in a lesser extent than that by H_2SO_4. It is also evident from its lower yield 41% and high BET surface area. The lower mechanical strength is understood from high macroporosity.

Effect of impregnation condition: As carbons prepared from palm kernel shell sinking in impregnation solution (wetted charge) have high macroporosity, attempts were made to study the effect of impregnation condition, charge state, on macroporosity development. Carbons, PSW-P-ad-500 and PSW-P-ed-450, were derived from charges apparently (semi-dried) and completely dried respectively by evaporation prior to carbonization and then compared with PSW-P-500, derived from wetted charge. The order of lowering the formation of macroporosity is: 47/31/12% by wetted, completely dried and apparently dried charge respectively. A rapid temperature rise at drying stage may cause higher macropore development in wet charge precursor. The BET surface area and total pore volume of PSW-P-ad-500 and PSW-P-ed-450 are 1476 and 1366 m^2/g and 0.8 and 0.75 cm^3/g respectively. This concludes that highly micro- and mesoporous carbon with high specific surface area could successfully be prepared from palm kernel and coconut shell using apparently dried charge.

Effect of precursor size: A carbon, PSWfg-P-450, prepared from smaller particle sizes, 1.18-0.60 mm, of palm kernel shell showed high N_2 adsorption at relatively low pressure. This indicates a major micropore contribution compared to the other, PSW-P-ed-450, derived from the same precursor but larger in particle sizes (2.36-1.18 mm). Prolong impregnation of both precursors, smaller and larger, (72 and 66 hours respectively) shows the BET and micropore surface areas as high as 1471 / 1366 and 547 / 154 m^2/g respectively. Prolong impregnation certainly intensified hydrolysis of lignocellulosic material[1] and thus vigorously weakened the raw material particles.

Materials of lower particle sizes are softer than that of larger particle since they were prepared by crushing. Moreover, as carbonizations were carried out in wetted condition, these softer particles were affected tremendously which in turn enhanced cracking (macroporosity 53%) in finished product. The higher destruction of volatile matters in case of smaller sized material was also evident from its lower yield (45%) compared to that of the other carbon prepared from larger particle sizes (50%).

Effect of carbonization temperature: Various carbons were prepared from chemical impregnated palm kernel and coconut shells using 1:1 ratio of raw material and H_3PO_4, by carbonizing at 400, 450, 500 and 700^0 C with a hold

time of one hour. The highly developed specific surface area (ca. 1500 m^2/g) and micro- and mesoporosity (total pore volume 0.72-0.94 cm^3/g) are observed in carbons obtained at carbonization temperatures of 450-500^0 C. Carbon prepared at temperatures 400 and 700^0 C showed BET surface area 592 and 734 m^2/g with a total pore volume 0.31 and 0.36 cm^3/g respectively. Carbonization at 400^0 C is too low to evolve volatile matter which is realized from its larger yield (68%) whereas high temperature (700^0 C) causes shrinkage of pores for which micropore volume is reduced extremely to 0.03 cm^3/g while showing micropore surface area even high 132 m^2/g. All carbons discussed here were prepared from 1:1 impregnation ratio.

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References

1. Hsisheng T. and Sheng-Chi W., Preparation of porous carbons from phenol-formaldehyde resins with chemical and physical activation, *Carbon,* **38,** 817-824 **(2000)**

2. Laine J., Effect of the preparation method on the pore size distribution of activated carbon from coconut shell, *Carbon,* **30,** 601-604 (**1992**)

3. Daud W. M. A. W., Ali W. S. W. and Sulaiman M. Z., The effects of carbonization temperature on pore development in palm-shell-based activated carbon, *Carbon,* **38**, 1925-1932 (**2000**)

4. Jankowska H., Swiatkowski A. and Choma, J., Active Carbon, Ellis Harwood Ltd., West Sussex, England, **(1991)**.

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